

Nonlinear optical properties of a self-organized dye thin film

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A self-organized thin film of a cyanine dye is fabricated by the spin-coating technique and is characterized by ultraviolet-visible spectroscopy, infrared (IR) spectroscopy, small-angle X-ray diffraction, ellipsometer, and atomic force microscopy (AFM). The nonlinear optical properties of the thin films are investigated by degenerate four wave mixing (DFWM) technique. The cyanine dye thin film sample exhibits high optical nonlinearities ($\chi^{(3)} = 2.55 \times 10^{-12}$ esu), and the mechanism is analyzed by the exciton coupling theory.

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The supra-molecular nanoarchitectures ranging from simple dimers to three-dimensional micro-crystals have currently received widespread attentions in fundamental and applied researches. As the potential materials for self-organization, cyanine dyes are considered as the key to advanced functional organic materials for xerography^[1], photography^[2], electronics and photonics^[3,4] and so on. As well known, the π -electron conjugation system gives rise to large optical nonlinearities (NLO)^[5,6], which is considered as the attractive candidates for all-optical switching, optical computing, bistable elements, and logic devices^[7]. A well-known aggregation of cyanine dyes is constructed as the simple one-dimensional stacks as the famous Jelley aggregates (J-aggregates), which can be approximately modelled by linear Frenkel chains^[8,9], and displays extraordinary peculiarities in their NLO responses^[10]. Hence, more and more cyanine dye self-aggregations are investigated for the NLO prosperities by means of various preparations, such as solutions^[11], Langmuir-Blodgett (LB) films^[12], single crystals^[13], and dispersed polymer films^[14]. However, to our knowledge, the structural factors governing their third-order nonlinear optical properties have not been thoroughly understood, which impedes the further applications of the cyanine dyes. In this paper, for the sake of the more understanding and application, the high density J-aggregates film of the cyanine dye 1,1'-diethyl-3,3',3'-tetramethyl-indolepentylmethinecyanine iodine (PC, see Fig. 1), with the large third-order nonlinear optical property, is fabricated on the silica substrate by a

simple spin-coating technique, and the thin film is characterized by ultraviolet-visible spectra, infrared (IR) spectra, small-angle X-ray diffraction, ellipsometer, and atomic force microscopy (AFM). The optical nonlinearities are measured by degenerate four wave mixing (DFWM) at the wavelength of 532 nm, and their mechanisms are theoretically analyzed.

The cyanine dye PC was synthesized by the procedure described in Ref. [15]. Its structure was identified by mass spectra (MS), ¹H nuclear magnetic resonance (¹H-NMR), IR spectra, and elemental analysis (EA). The cyanine dye PC solution was dropped onto the silica substrate, which was sonicated in acetone and deionized water for 30 min, and excess solution was removed by spinning (500 rpm for 9 s and 1500 rpm for 50 s by CHEMAT Spin-coater KW24A). With the evaporation of 2,2,3,3-tetrafluoro-1-propanol (TFP), the remainder formed a thin film on the substrate, and its thickness depended on the speed of rotation and the concentration of the solution.

The absorption spectra were measured by Hitachi U-3000 spectrometer. Fourier-transform (FT) IR spectra were measured by Nicolet Nexus 670 FT spectrometer. Small-angle X-ray diffraction was analyzed by Rigaku D/Max 2550 VB/PC X-ray diffraction. The morphology of the film was observed by SPA300HV AFM microscopy, and the surface roughness was observed with digital instruments scanning probe microscope with a multi-mode head in air. The film thickness d and refractive index n were measured by ZD-003 ellipsometer at a wavelength of 633 nm. The optical nonlinearities were investigated by the DFWM technique with a Nd:YAG laser (Continuum model YG601) with the pulse width of 35 ps, the wavelength of 532 nm and the repetition rate of 10 Hz. The DFWM signal was acquired by Boxcar SR250 (Stanford Research System, Inc.) and recorded by a computer. Compared with a reference sample of carbon disulfide (CS₂), the third-order nonlinear susceptibility $\chi^{(3)}$ of the cyanine PC was obtained as

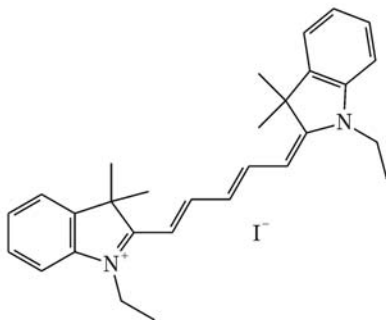


Fig. 1. Molecular structure of the cyanine dye PC.

$$\chi^{(3)} = \sqrt{\frac{I}{I_r}} \frac{l_r}{l} \left(\frac{n}{n_r} \right)^2 \left\{ \frac{a l e^{\frac{1}{2} a l}}{1 - e^{-a l}} \right\} \chi_r^{(3)}, \quad (1)$$

$$n_2 = \frac{12\pi}{n} \chi^{(3)}, \quad (2)$$

where I means the intensity of DFWM signal, α corresponds to the absorptive index, l is the interaction length, and n is the linear refractive index. The subscript “r” means the counterpart of the reference sample with the $\chi^{(3)}$ of 6.8×10^{-13} esu for CS₂ at the wavelength of 532 nm^[16].

The AFM images and ellipsometer should be the effective tools for the surface roughness and thickness. The thickness of the thin film is measured to be about 252 nm. As shown in Fig. 2, the thin film surface of the cyanine dye appears very smooth and the roughness is less than 2 nm. It clearly shows the corresponding surface morphology of the cyanine dye PC thin film.

Figure 3 depicts the absorption spectra of the PC solution and the thin film, respectively. The absorption peak of the PC solution is observed at 639 nm for the π - π^* transition from the ground state S_0 to the first excited state S_1 , and there exists a weak hypsochromic vibronic side band, which may be ascribed to the vibronic splitting of the singlet excited state^[17]. However, the absorption spectrum is widened, and the obvious red-shift of 40 nm is observed from the solution to the thin film. It can be attributed to the PC J-aggregates formation. Based on the exciton coupling theory^[18], the formation of J-aggregates will induce the interaction energy V due to the inter-molecular coupling. On the one hand, the first excited-band should be widened for four times the interaction energy V between the molecules in the chain, and so the greater inter-molecular assemblage results in the larger bandwidth.

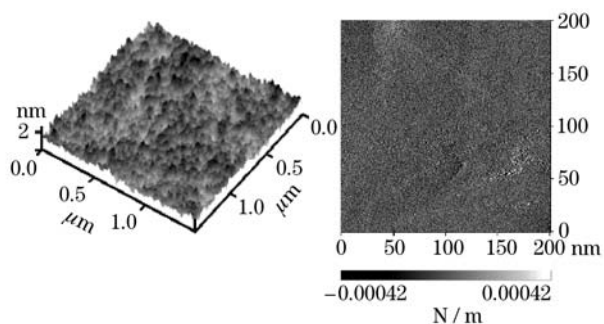


Fig. 2. Surface morphology of the cyanine dye PC thin film.

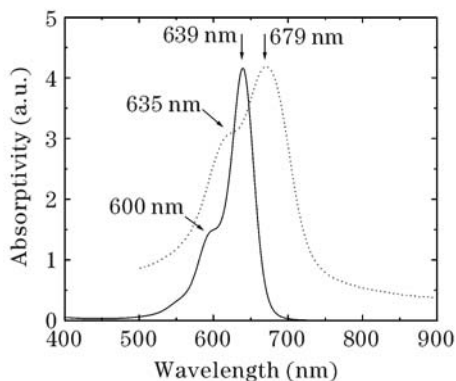


Fig. 3. Absorption spectra for the PC solution (solid line) and thin film (dotted line).

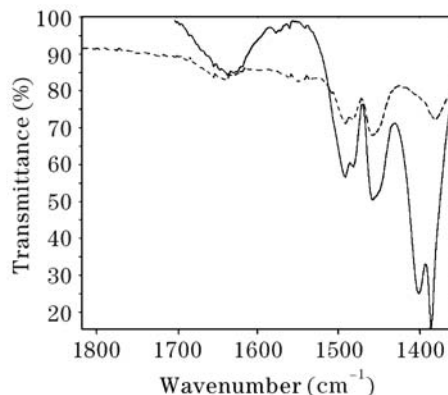


Fig. 4. IR spectra for the cyanine dye PC powder (solid line) and thin film (dashed line).

interaction energy V is negative in J-aggregation, and then the excited band shifts to the lower level. Consequently, compared with the PC monomer, the spectrum of the thin film shows a broadband as well as red-shift.

Figure 4 shows the IR spectra for the cyanine dye PC powder and self-organized thin film in the region from 1350 to 1850 cm^{-1} . The bands at 1625 and 1500 cm^{-1} are associated with the anti-symmetric and symmetric stretching vibrations of C=C and C=N bonds, respectively. The band near 1450 cm^{-1} is attributed to the bending mode of CH₃ connected to N atom, and the bands at 1400 and 1380 cm^{-1} for the bending vibration of H₃C—C—CH₃. The IR peaks for the PC dye powder and the self-organized thin film are observed at the same wavenumber, which indicate that the substrate has no influence on the conformation of the PC molecules during the process of self-assembling. However, the increases of the steric hindrance, induced by the “head-to-tail” PC aggregate, results in decreasing the relative intensities of the bands at 1400 and 1380 cm^{-1} for H₃C—C—CH₃ to the band near 1450 cm^{-1} for the bending mode of CH₃ in self-organized thin film.

The J-aggregate thin film is also validated by the small-angle X-ray diffraction measurement. As shown in Fig. 5, the Bragg diffraction peak indicates the existence of an ordered multilayer structure in the self-organized cyanine dye PC thin film. The interlayer spacing of 6.67 nm, obtained from diffraction peak, also suggests that PC has an edge-on conformation through the electrostatic absorption between iodine ions and the substrate^[19]. The

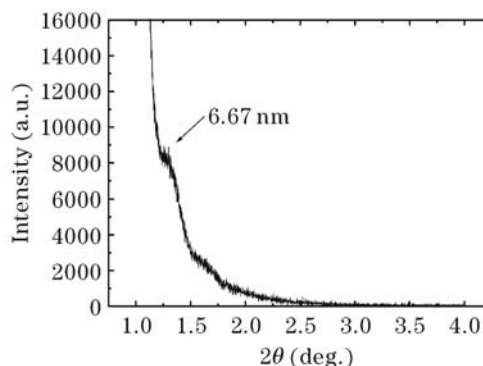


Fig. 5. X-ray diffraction patterns for the cyanine dye PC thin film.

Table 1. Optical Characteristics for the Cyanine Dye PC (the Concentration of 1×10^{-5} mol/L)

	λ_{\max} (nm)	$\chi^{(3)}$ (esu)	n_2 (esu)	γ (esu)
PC Solution	639	3.4×10^{-13}	9.5×10^{-12}	2.3×10^{-29}
PC Thin Film	678	2.55×10^{-12}	3.7×10^{-11}	6.3×10^{-28}

value of tilt angle α is $\cos^{-1}((66.7/2)/d_s)$, which is between the long axis of the cyanine dye PC molecules and the substrate surface. And, the calculated value of d_s can be obtained by approximatively summing the bond lengths of whole molecule PC, including two benzene rings, the bond length projections of C—N, C=N, and $(m+2)$ times the C—C, C=C, and C—H bond lengths projected on the framework of molecule PC, where m is the number of the bonds in PC^[20]. So, the tilt angle (α) is $\cos^{-1}(33.4/49.1) = 47.2^\circ$, satisfying the need of J-aggregate^[21].

The values of near-resonance $\chi^{(3)}$ and the nonlinear refractive index are measured by DFWM technique and listed in Table 1. As shown in Table 1, the cyanine dye PC in the thin film has high third-order optical nonlinearities, and second order molecular hyperpolarizability γ for the cyanine dye PC in the J-aggregate is observed to be enhanced by nearly ten times.

Under the condition of the near-resonance and centrosymmetric structure of sample, π -electron delocalization of the pentamethine unit in backbone of dye PC is firstly responsible for the third-order nonlinear optical property $\chi^{(3)}$, which could follow the equation^[22]

$$\chi^{(3)} \propto \gamma \propto \frac{\mu_{01}^4}{E_{01}^3}, \quad (3)$$

where γ stands for the second-order hyperpolarizability, E_{01} and μ_{01} are the energy difference and the transition dipole moment between the ground states and the first excited states, respectively. For the π -conjugation backbone end capped with two indole groups, the donor and acceptor are not strong enough to induce the observable intra-molecular charge transfer (ICT) that could evoke the bands to be obviously red-shifted in IR spectrum^[23]. However, the little difference of the electronic densities between the indole groups will induce the inter-molecular head-tail coupling and the formation of the J-aggregates, and then the PC dye thin film can be self-organized in the course of spin-coating. The formation of the “head-to-tail” aggregate can result in the increases of the steric hindrance of $\text{H}_3\text{C}-\text{C}-\text{CH}_3$'s bending vibration. So, the relative intensity of the IR absorption bands for the bending vibration of $\text{H}_3\text{C}-\text{C}-\text{CH}_3$ decreases in the self-organized thin film, which supports our hypothesis of J-aggregates structure very well. According to Ref. [24], the one-dimensional J-aggregates PC, characterized by a main head-to-tail interaction between transition dipoles, can be described as an ensemble of identical collinear oscillating dipoles. We consider the J-aggregates PC as a linear chain of N identical dipoles with the two-level model, i.e., a ground state and a one-excited band with various k -states. The width of the one-excited band depends on the inter-molecular interaction energy V . The

oscillator strength f_k is proportional to μ_k^2 , where μ_k^2 is the transition dipole moment to the k th energy level in the excited band^[24],

$$f_k \propto \mu_k^2 = \frac{2\mu_{\text{mon}}^2}{N+1} \cot^2\left(\frac{k\pi}{2(N+1)}\right), \quad k = \text{odd},$$

$$f_k = 0, \quad k = \text{even}, \quad (4)$$

where μ_{mon}^2 is the contributing component of the transition dipole moment in the monomer molecules PC. So, the states with an odd quantum number k have oscillator strength (transition dipole moment squared), and hence their absorption band appears in the visible region (see Fig. 3). It is revealed that the state with $k=1$ contains by far the most oscillator strength up to $0.81(N+1)\mu_{\text{mon}}^2$ for $N \gg 1$, which is about 81% of the total oscillator strength from the ground state to one-excited state transition, whereas the oscillator strengths of higher states drop off as $1/k^2$ for $k \ll N$ ^[25]. Then Eq. (4) could be deduced as

$$f_1 \sim \mu_1^2 = \frac{8(N+1)\mu_{\text{mon}}^2}{\pi^2}, \quad N \gg 1. \quad (5)$$

Therefore, considering Eq. (3), $\chi^{(3)}$ and γ are in proportion to N^2 ,

$$\chi^{(3)} \propto \gamma(-\omega, \omega, -\omega, \omega) \propto \frac{(N+1)^2 \mu_{01}^4}{E_{01}^3} \propto N^2. \quad (6)$$

However, it is well known that the third-order nonlinear susceptibility for the molecules in non-aggregation is in proportion to the number of molecules^[26],

$$\chi^{(3)} \propto \gamma(-\omega, \omega, -\omega, \omega) \propto N. \quad (7)$$

Therefore, according to Eqs. (3), (6), and (7), it could be deduced that the larger $\chi^{(3)}$ of PC in thin film than that in monomer is ascribed to the collective behavior of the J-aggregation. For the centro-symmetric cyanine dye, the third-order nonlinear optics can be remarkably improved by forming a certain regulated organization (J-aggregates) with the inter-molecular electrostatic interaction. The nature of the enhancement stems from a size-enhanced response. Because in monomers the molecules do not interact, the scaling of $\chi^{(3)}$ is just linear with size $\sim N$. By contraries, in J-aggregation $\chi^{(3)}$ contains terms which scale as $\sim N^2$ under the condition of near-resonance.

In conclusion, an ultrathin multilayer film containing the cyanine dye PC has been prepared by the spin-coating technique on a quartz substrate, and its properties are investigated by ultraviolet/visible spectroscopy, IR spectra, small-angle X-ray diffraction, ellipsometer, and AFM images. Compared with the cyanine dye PC powder, the thin film has higher third-order nonlinear optical properties, which is attributed to π -electron delocalization of the pentamethine unit and enhanced by the inter-molecular exciton-exciton coupling. The large third-order nonlinear optical properties and the excellent processability show that they are the promising candidates to be developed for the optical switching devices.

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